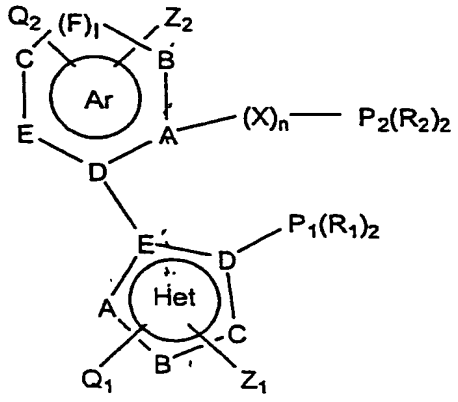
CLAIMS

1. An atropo-isomeric chiral phosphorated ligand of formula (I), having C_1 symmetry, in the optically active form or in the racemic form



(I)

wherein

the atoms A, B, C, D, E and F, equal to or different from one another, are carbon atoms or hetero-atoms chosen from among oxygen, nitrogen and sulphur, which form together an Ar of Het aromatic residue, where Ar is chosen between pentatomic heterocyclic residue and phenyl, and Het is a pentatomic heterocyclic residue, and where said pentatomic heterocyclic aromatic residue contains 1 or 2 hetero-atoms, equal to or different from one another, selected from the group consisting of -O-, -S- and $-NR_3-$, wherein R_3 = H, an alkyl group, an aromatic group, a group $-P_1(R_1)_2$, or a nitrogen atom comprised as hetero-atom in the other pentatomic heterocyclic residue belonging to the structure of formula (I) ;

l = 0, 1 ; when l =1, F is a carbon atom ;

R_1 and R_2, bound to the phosphorous atoms, equal to or different from one another, are selected from a linear, branched or cyclic C_3-C_{10} alkyl group, a carbocyclic aromatic group, and a heterocyclic aromatic group having 5-6 members in the cycle, containing one or more hetero-atoms chosen among oxygen, sulphur and nitrogen, where said carbocyclic or heterocyclic aromatic group is optionally substituted with one or more groups selected from a linear or branched C_1-C_{10} alkyl group, a linear or branched C_1-C_{10} alkoxyl group, an halogen, $-COOR_4$, $-SO_3R_4$ and $-NR_5R_6$, where

R_4 is chosen among H, alkyl, aryl, alkaline or alkaline-earth metal, $-NH_4^+$ and alkyl ammonium cation having from 4 to 20 carbon atoms; and where R_5 and R_6, equal to or different from one another, are H or alkyl ; or

R_1 and R_2 together with the phosphorus atom, form a heterocycle having 3-6 atoms in the cycle, optionally substituted with linear or branched C_1-C_{10} alkyl groups ;

X is an -O- group or an $-N(R_7)-$ group, where R_7 is chosen among H, alkyl and phenyl ;

n is 0 or 1, when Ar is a heterocyclic aromatic residue ;

n is 1, when Ar is phenyl ;

Q_1, Q_2, Z_1 and Z_2, equal to or different from one another, are selected from the group consisting of H, linear, branched or cyclic C_1-C_{10} alkyl, linear or branched C_1-C_{10} alkoxyl, phenyl and halogen, or

Q_1 taken together with Z_1, or Q_2 taken together with Z_2, form a carbocyclic aromatic ring selected from phenyl and naphthyl, said carbocyclic aromatic ring being optionally substituted with one or more T groups, where T is chosen among halogen, C_1-C_{10} alkyl, C_1-C_{10} alkokyl, $-COOR_4$, $-SO_3R_4$ and $-NR_5R_6$, where R_4 is selected from H, C_1-C_{10} alkyl, phenyl, alkaline or alkaline-earth metal, $-NH_4^+$ or C_4-C_{12} alkyl ammonium cation, and where R_5 and R_6, equal to or different from one another, are selected from H and C_1-C_{10} alkyl ; and wherein

$-P_1(R_1)_2$ and $-(X)_n-P_2(R_2)_2$ are bound to the corresponding carbocyclic or heterocyclic aromatic residue by means of a carbon atom of said aromatic residue or by means of a nitrogen atom comprised as hetero-atom in a pentatomic heterocyclic residue ;

said phosphorated ligand further having :

i) a difference between the residual charges of the phosphorous atoms

$$\Delta Q(P) = Q(P_1) - Q(P_2) > 0.05,$$

where $Q(P_1)$ and $Q(P_2)$ are the values of difference between the number of valence electrons and the number of electrons actually present for the phosphorous atoms P_1 and P_2, said difference between residual charges being calculated using the program MOPAC, Version 6.0, Method MNDO ;

ii) a cone angle β_n ("natural bite angle" according to Casey) ranging from 80° to

130°, defined as preferred chelation angle P_1-M-P_2 between the phosphorous atoms P_1 and P_2 and a transition metal M, said angle being obtained by minimization of the strain energy of the fragment M(diphosphine), where M is Rh, and calculated by means of the program SYBYL, using the force field of TRIPOS modified by entering the parameters developed for the Rh-diphosphine complexes by M. Kranenburg et al., in *Organometallics*, 14, 3081 (1995) ;

iii) an energy barrier value of interconversion between the two enantiomers of a given ligand

$$\Delta E = E_{trans} - E_{min} \geq 28 \text{ Kcal/mol},$$

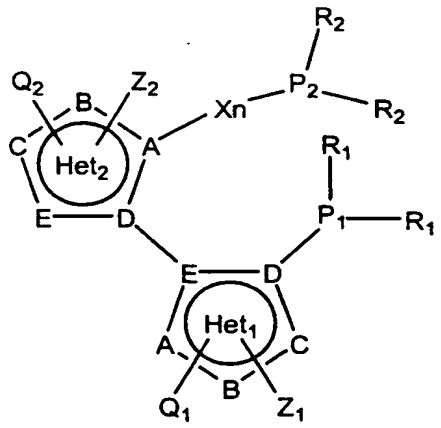
where E_{trans} is the energy value for the transition state, and E_{min} is the value associated to the state of minimum energy of the enantiomers, expressed in Kcal/mol, said ΔE being calculated by using the program MOPAC, Version 6.0, Method MNDO, assuming that the energy of the maximum-energy conformer E_{trans} is that of the conformer in which the two aromatic rings are coplanar.

2. The phosphorated ligand according to claim 1, wherein

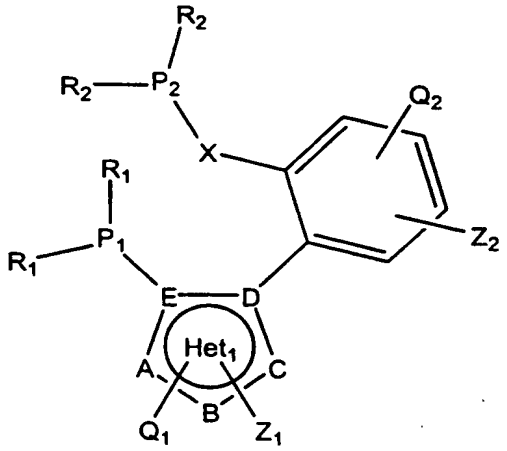
i) said difference $\Delta Q(P) = Q(P_1) - Q(P_2)$ is > 0.15 ;

ii) said "natural bite angle" β_n ranging from 83° and 120°.

3. The phosphorated ligand according to claim 1, wherein said phosphorated ligand is chosen between a ligand of formula (I)a and a ligand of formula (I)b :



(I)a



(I)b

where

Het_1 and Het_2 are pentatomic heterocyclic aromatic rings, equal to or different from one another, defined as Het in claim 1 ;

n is 0 or 1 ;

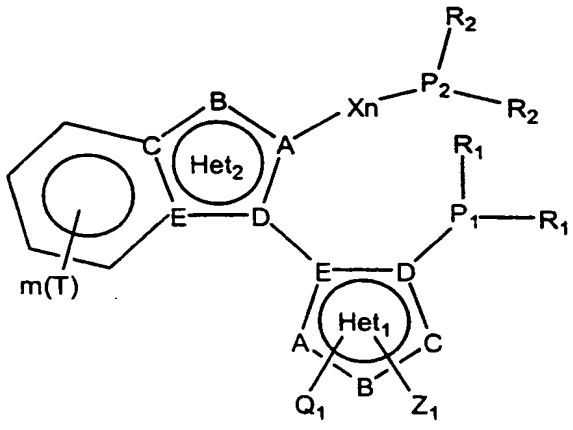
X, A, B, C, D, E, Q_1, Q_2, Z_1 and Z_2 are as defined in claim 1.

4. The phosphorated ligand according to claim 1, wherein said heterocyclic residue is selected from the group consisting of thiophene, pyrrole, furan, imidazole, isoxazole, isothiazole, pyrazole and triazole.

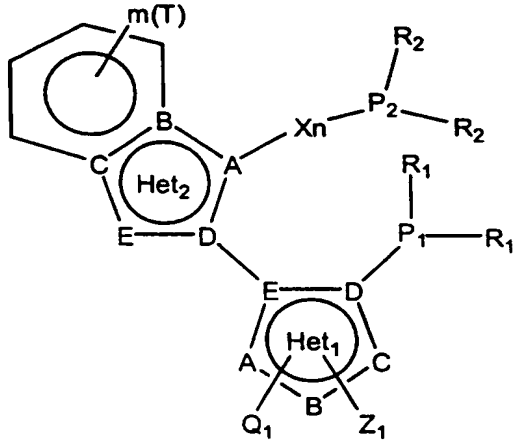
5. The phosphorated ligand according to claim 1, wherein Q_1 taken together with Z_1, or Q_2 taken together with Z_2, form a carbocyclic ring, and Het is condensed with phenyl or naphthyl.

6. The phosphorated ligand according to claim 5, wherein said heterocyclic ring Het condensed with phenyl is selected from the group consisting of benzothiophene, naphthothiophene, indole, benzofuran and benzoimidazole.

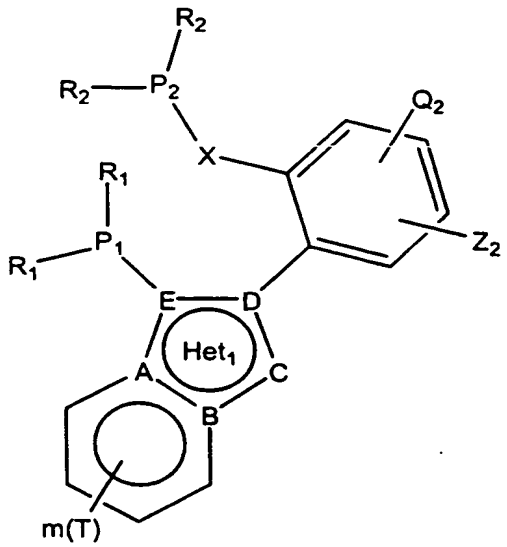
7. The phosphorated ligand according to claim 1, wherein said phosphorated ligand is chosen from a ligand of formula (I)c, (I)d and (I)e :



(I)c



(I)d



(I)e

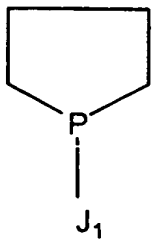
wherein Het_1 and Het_2 are defined as Het in claim 1 ;

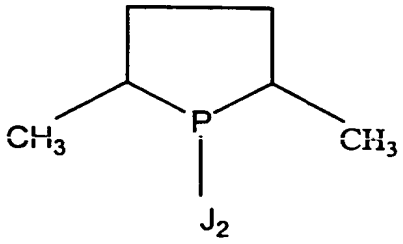
A, B, C, D, E, Q_1, Z_1, P_1, R_1,Q_2, Z_2, P_2, R_2 and T are as defined in claim 1 for formula (I) ;

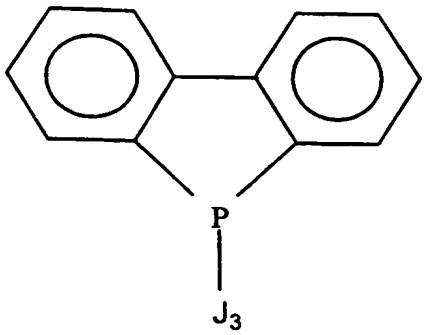
m is 0, 1 or 2.

8. The phosphorated ligand according to claim 1, wherein said heterocyclic aromatic residue is selected from the group consisting of 2,5-dimethyl-thien-3-yl, 4,6-dimethyl-benzofur-3-yl, 3-methyl-indol-2-yl, 1-N-methyl-indol-2-yl, and benzothien-3-yl ; and said carbocyclic aromatic residue is phenyl.

9. The phosphorated ligand according to claim 1, wherein said groups $-P_1(R_1)_2$ and $-P_2(R_2)_2$ are selected from diphenyl phosphine, dicyclohexyl phosphine, J_1, J_2 and J_3 , where J_1, J_2 and J_3 have the following formulas :

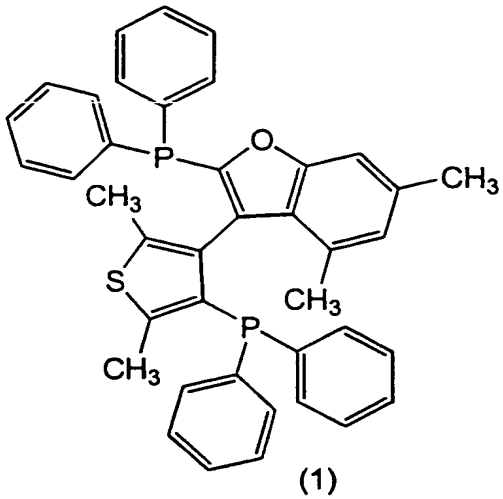




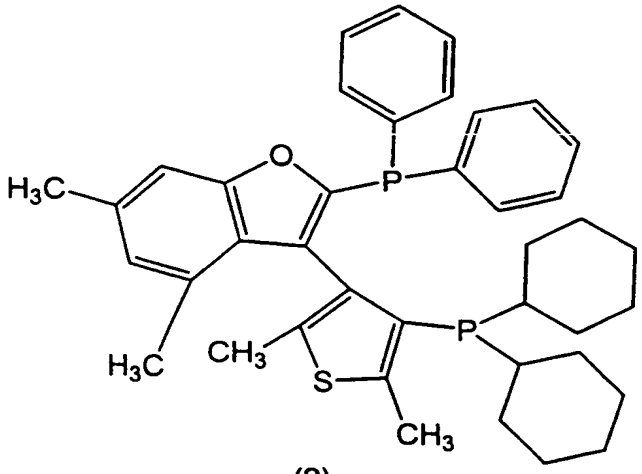


10. The phosphorated ligand according to claim 1, containing one of the following sub-structures : (4-diphenylphosphine)- or (4-dicyclohexylphosphine)-2,5-dimethyl-thien-3-yl ; (1-N-diphenylphosphine)- or (1-N-dicyclohexylphosphine)-3-methylindol-2-yl; (3-diphenylphosphine)- or (3-dicyclohexylphosphine)-1-N-methylindol-2-yl; 2-(diphenylphosphine)- or 2-(dicyclohexylphosphine)-benzothien-3-yl; 2-(diphenylphosphine-oxy)- or 2-(dicyclohexylphosphine-oxy)-phenyl-1-yl ; 4-(diphenylphosphine-oxy)- or 4-(dicyclohexylphosphine-oxy)-2,5-dimethyl-thien-3-yl ; 4-(2',5'-dimethyl-phospholyl)- or 4-(dibenzophospholyl)-2,5-dimethyl-thien-3-yl ; 1-N-(2',5'-dimethyl-phospholyl)- or 1-N-(dibenzophospholyl)-3-methyl-indol-2-yl.

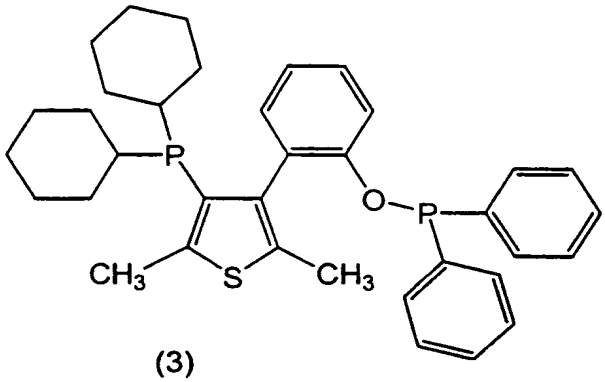
11. The phosphorated ligand according to claim 1, wherein said phosphorated ligand is chosen from the compounds from (1) to (15).



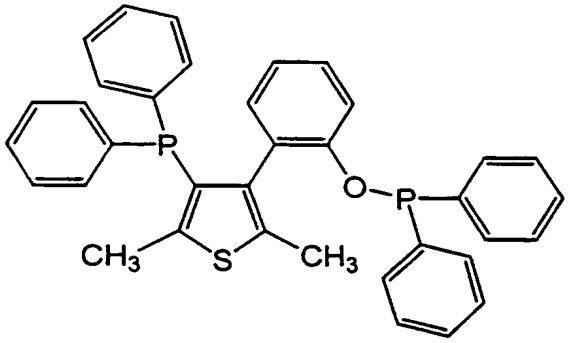
(1)



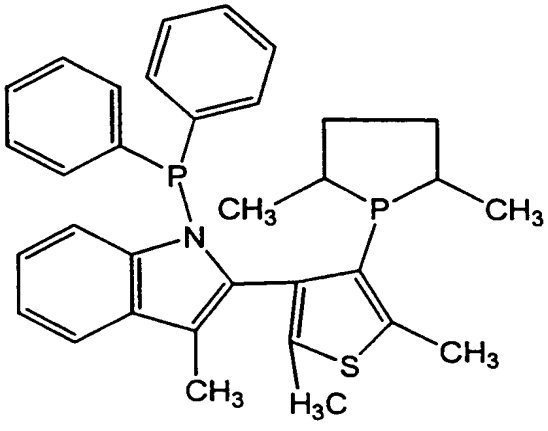
(2)



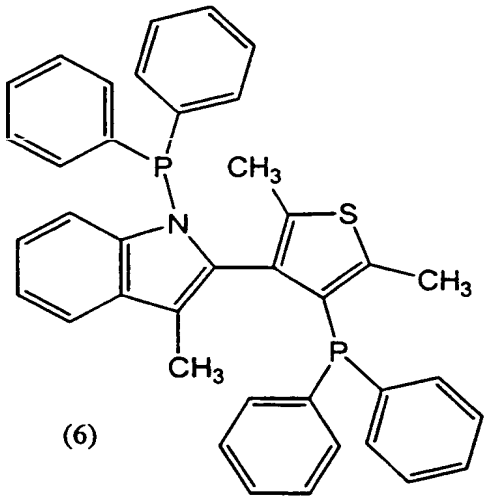
(3)



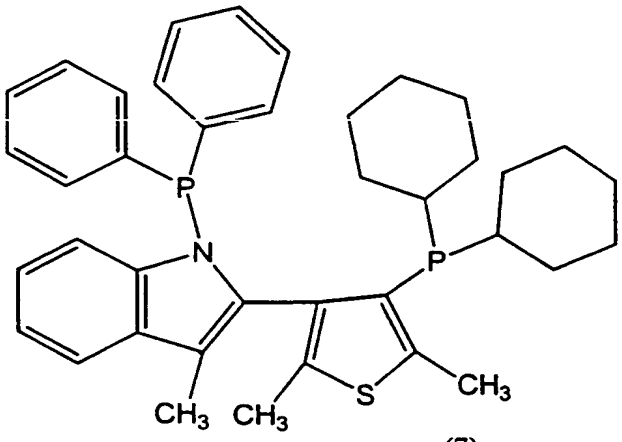
(4)



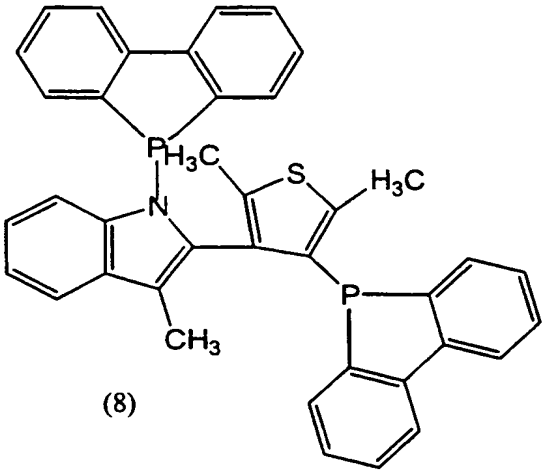
(5)



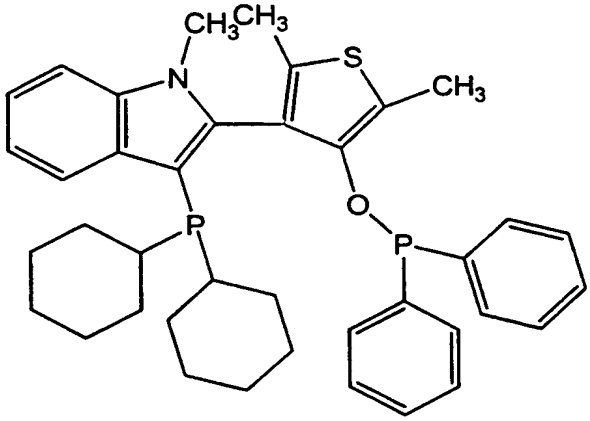
(6)



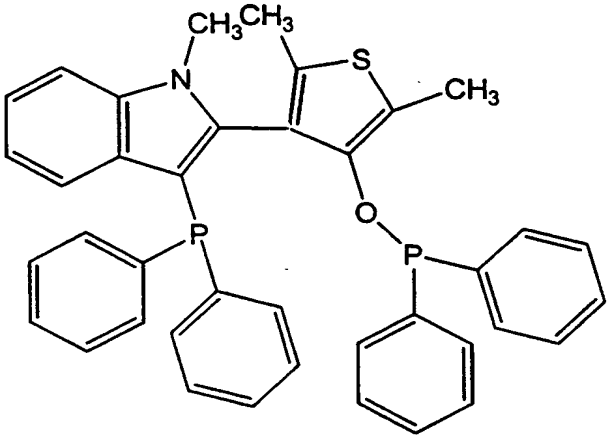
(7)



(8)

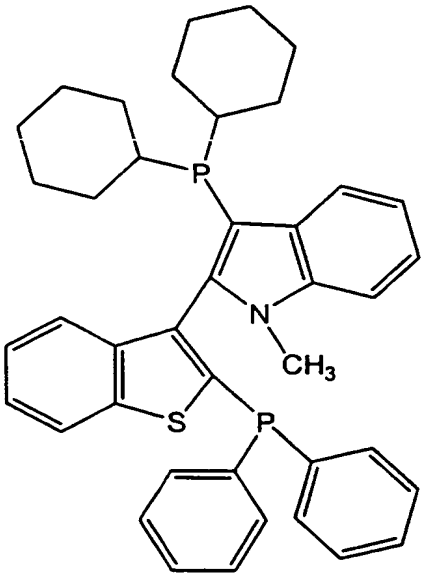


(9)

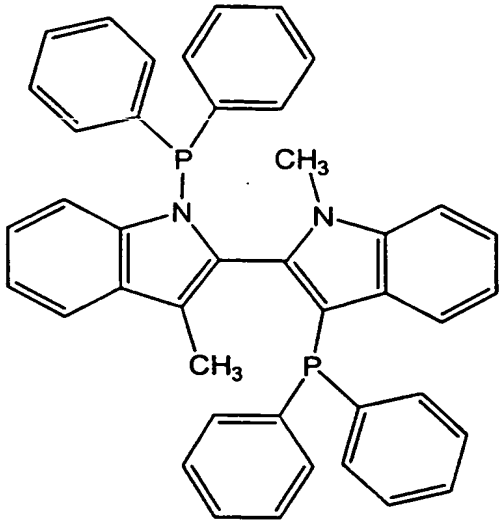


(10)

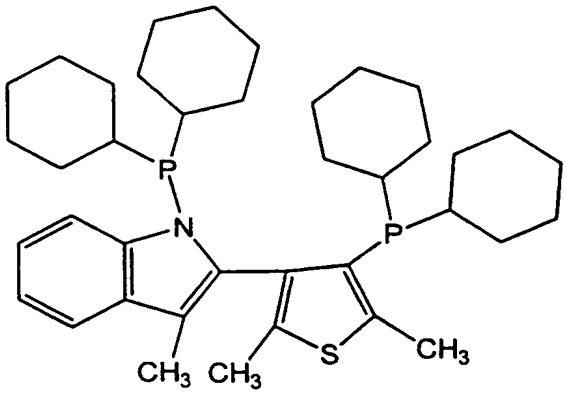
13



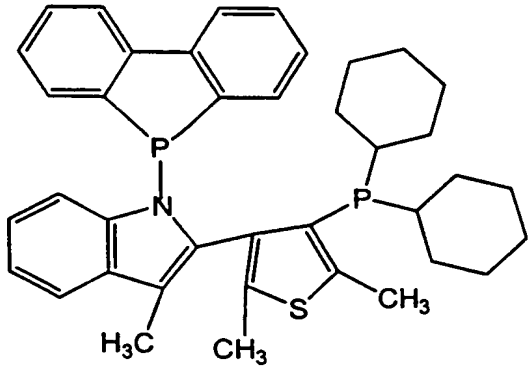
(11)



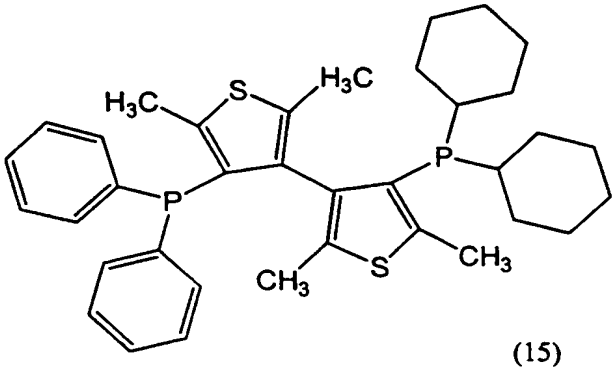
(12)



(13)



(14)



(15)

12. Procedure for the preparation of an atropo-isomeric phosphorated ligand of formula (I) having C_1 symmetry, as defined in claim 1, comprising the following steps :

a) construction of the molecular model of a series of structures of ligands of formula (I), $(I)_1$, $(I)_2$, $(I)_3$, ---, $(I)_z$, where z is the number of structures created, by means of the computation program SYBYL, Version 6.2 ;

b) conformational analysis, comprising the determination of the minimum-energy conformer for each structure from $(I)_1$ to $(I)_z$, followed by optimisation using the program MOPAC, Version 6.0, Method MNDO ;

c) calculation of the difference

$$\Delta Q(P) = Q(P_1) - Q(P_2)$$

as defined in claim 1, for each minimum-energy conformer structure, by using the computation program MOPAC, Version 6.0, Method MNDO ;

d) calculation, for each structure from $(I)_1$ to $(I)_z$, of the value of the energy barrier of interconversion between the two enantiomers (atropo-isomers) of formula (I)

$$\Delta E = E_{trans} - E_{min}$$

as defined in claim 1, made using the computation program MOPAC, Version 6.0, Method MNDO, assuming that the value E_{trans} is that of the maximum-energy conformer having the two rings Ar and Het of the structure (I) coplanar with respect to one another ;

e) calculation, for each structure from $(I)_1$ to $(I)_z$, of the "natural bite angle" β_n, as defined in claim 1, obtained by minimisation of the strain energy of the fragment M(diphosphine), imposing that M should be Rh and that the bending constant of the bond P_1-M-P_2 should be 0 Kcal mol^{-1}, and calculated by using the program SYBYL, Version 6.2, adopting the parameters of the force field of the program TRIPOS, modified by entering the parameters developed for the Rh-diphosphine complexes by M. Kranenburg et al., in *Organometallics*, 14, 3081, 1995 ;

f) selection of the structures from $(I)_1$ to $(I)_z$ having :

i) $\Delta Q(P) = Q(P_1) - Q(P_2) > 0.05$

i) a "natural bite angle" β_n ranging between 80° and 130° ;

ii) an energy barrier of interconversion between the two enantiomers of the same structure $\Delta E \geq 28$ Kcal/mol;

g) chemical synthesis of the phosphorated ligands of formula (I) thus selected.

13. The procedure according to claim 12, wherein said step f) consists in a selection of the structures from $(I)_1$ to $(I)_z$ having :

i) the difference $\Delta Q(P) = Q(P_1) - Q(P_2) > 0.15$;

ii) the "natural bite angle" β_n ranging between 83° and 120°.

14. The procedure according to claim 12, wherein said step g) is carried out according to one of the following procedure :

A) coupling reaction between aromatic or hetero-aromatic halides with organometallic aryl or hetero-aryl reactants selected from organolithium, organomagnesium, organozinc, and organoboron, in the presence of catalytic quantities of salts or complexes of copper, nickel, or palladium; or

B) cyclisation and aromatisation, with formation of one of the two heterocyclic rings comprised in the structure of formula (I), of a precursor already containing the other heterocyclic or carbocyclic system ;

in said procedure the introduction of the groups containing the phosphorous atom preceding or following the reaction of formation of the inter-annular bond.

15. The procedure according to claim 14, wherein said introduction of the groups containing the phosphorous atom is carried out according one of the following reactions :

in the case of phosphine derivatives :

$Ar\text{-}[M] + XP(R_1)_2 \rightarrow Ar\text{-}P(R_1)_2$

$Ar\text{-}[M] + XP(=O)(R_1)_2 \rightarrow Ar\text{-}P(=O)(R_1)_2 \rightarrow Ar\text{-}P(R_1)_2$

$Ar\text{-}[M] + (R_2O)_2P(=O)(R_1) \rightarrow Ar_2\text{-}P(=O)(R_1) \rightarrow Ar_2\text{-}PR_1$

$Ar\text{-}X + ZP(R_1)_2 \rightarrow Ar\text{-}P(R_1)_2$

wherein

Ar is an aromatic residue comprised in the structure of formula (I) ;

[M] is an organometallic group ;

X is a halogen ;

Z is an alkaline metal ;

R_1 and R_2 are alkyl or aryl residues ;

- in the case of phosphite or aminophosphine derivatives :

$Ar\text{-}OH + XP(R_1)_2 \rightarrow Ar\text{-}OP(R_1)_2$

$Ind\text{-}NZ + XP(R_1)_2 \rightarrow Ind\text{-}NP(R_1)_2$

$Ind\text{-}NZ + XP(=O)(R_1)_2 \rightarrow Ind\text{-}NP(=O)(R_1)_2 \rightarrow Ind\text{-}NP(R_1)_2$

$Ar\text{-}NHR_2 + XP(R_1)_2 \rightarrow Ar\text{-}NR_2P(R_1)_2$

$Ar\text{-}X + ZOP(R_1)_2 \rightarrow Ar\text{-}OP(R_1)_2$

Ar is a carbocyclic aromatic or hetero-aromatic residue comprised in the structure of formula (I) ;

Ind is an indole residue ;

X is a halogen ;

Z is an alkaline metal ;

R_1 is an alkyl or aryl group ;

R_2 is H or an alkyl or aryl group.

16. The procedure according to claim 14, further comprising the resolution of a ligand of formula (I) into its optical antipodes, via separation on chromatographic column or through a membrane, using a chiral stationary substrate or a chiral eluent, or via fractioned crystallisation of a corresponding diastereo-isomeric adduct.

17. The procedure according to claim 16, wherein, if the ligand of formula (I) comprises basic or acidic groups, the diastereo-isomeric adduct is the corresponding salt with an entantiomerically pure chiral acid or base; alternatively, the said adduct is the diastereo-isomeric salt between an enantiomerically pure chiral acid and the phosphinoxide corresponding to the present phosphorated ligand. In this case, the optical resolution is followed by reduction of optically active phosphinoxides into phosphines, via treatment with a reducing agent.

Sub A1

18. An organometallic complex, comprising a chiral phosphorated ligand of formula (I) as defined in each of the claims from 1 to 11, in the enanatiomerically pure or enriched form, and a transition metal.

19. The organometallic complex according to claim 18, wherein the transition metal is selected from the group consisting of Rh, Ru, Ir, Pt, Pd and Ni.

20. Use of an organometallic complex according to claim 18 for the preparation of an optically active chiral catalyst.

21. Procedure for the preparation of an organic compound in the form of stereo-isomer, comprising at least one stereoselective reaction conducted in the presence of at least one organometallic complex as defined in claim 18.

22. The procedure according to claim 21, wherein said stereoselective reaction is

selected from the group consisting of enantio- and/or diastereoselective reactions of reduction, hydroformylation, hydroboration, hydrosilylation, hydrocyanation, allylation, vinylation and other reactions of formation of the C-C bond.